SUR LA SOLUBILITÉ MUTUELLE ENTRE LA FLAVONE ET SES DERIVÉS.

Par Tei-ichi ASAHINA et Kôichi YOKOYAMA.

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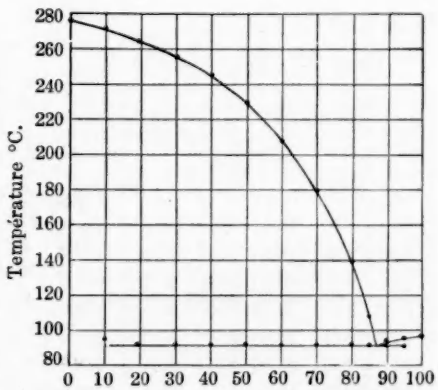
Dans un autre mémoire précedent,[1] l'un de nous a constaté de l'existence de solution solide entre la primétine et la flavone. Maintenant on est à examiner s'il y a de telle existence entre la flavone et ses derivés hydroxylés qui sont fréquentés dans la nature comme constituants des plantes. Nous avons fait des études sur les oxyflavones suivantes et, en même temps, sur quelques derivés acétylés et méthylés des oxyflavones. Cependant, nous n'avons pas observé la possibilité d'existence de solution solide jusqu'ici et la solubilité mutuelle des flavones dans l'état solide n'est rien de chose générale. La méthode adoptée est de même que celle précedente.

I. Etude du système: Chrysine (5,6-dioxyflavone) et flavone.

Table 1. (Voyez la Fig. 1.)

Pourcentages		Points de dégel °C.	Points de congel °C.
de flavone	de chrysine		
mg.	mg.		
0.0 —	100.0 —	—	275.0
10.0 (1.5)	90.0 (13.5)	95.0	271.0
19.3 (3.1)	80.7 (13.0)	91.5	264.0
30.0 (4.5)	70.0 (10.5)	91.5	255.0
40.0 (6.0)	60.0 (9.0)	91.5	245.0
50.0 (7.0)	50.0 (7.0)	92.0	229.0
60.0 (9.0)	40.0 (6.0)	91.5	208.0
70.0 (10.5)	30.0 (4.5)	91.5	180.0
80.0 (12.0)	20.0 (3.0)	91.5	139.0
85.0 (8.5)	15.0 (1.5)	91.5	108.0
90.0 (13.5)	10.0 (1.5)	92.0	94.5
95.0 (9.5)	5.0 (0.5)	91.3	95.2
100.0 —	0.0 —	—	96.5



Point eutéctique :
91.6°C., 87% de flavone.

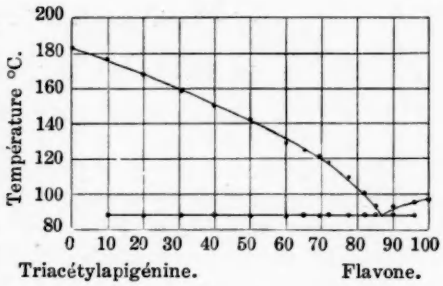
Fig. 1.

(1) T. Asahina, *Acta Phytochimica*, **7** (1933), 187.

II. Etude du système: Triacétylapigénine (5,7,4′-triacétoxyflavone) et flavone.

Table 2. (Voyez la Fig. 2.)

Pourcentages		Points de dégel °C.	Points de congel °C.
de flavone	d'acétyl-apigénine		
mg.	mg.		
0.0 —	100.0 —	—	183.3
10.0 (1.2)	90.0 (10.8)	88.5	176.8
20.0 (2.4)	80.0 (9.6)	88.0	168.0
30.0 (3.7)	69.4 (8.4)	88.0	158.5
40.0 (6.0)	60.0 (9.0)	88.0	150.2
50.0 (6.0)	50.0 (6.0)	88.0	142.0
60.0 (7.2)	40.0 (4.8)	88.0	129.0
65.0 (6.5)	35.0 (3.5)	88.0	125.0
69.4 (8.4)	30.6 (3.7)	88.0	122.2
71.7 (7.6)	28.3 (3.0)	88.0	118.0
77.4 (9.6)	22.6 (2.8)	88.0	109.5
82.0 (16.4)	18.0 (3.6)	88.2	101.0
85.0 (8.5)	15.0 (1.5)	88.0	93.0
90.0 (10.8)	10.0 (1.2)	88.0	93.0
96.0 (14.4)	4.0 (0.6)	88.0	95.0
100.0 —	0.0 —	—	96.5



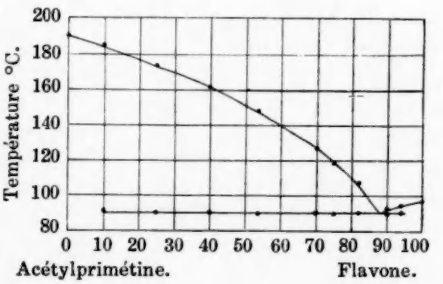
Point eutéctique :
88.0°C., 87% de flavone.

Fig. 2.

III. Etude du système: Diacétylprimétine (5,6-diacétoxyflavone)[2] et flavone.

Table 3. (Voyez la Fig. 3.)

Pourcentages		Points de dégel °C.	Points de congel °C.
de flavone	d'acétyl-primétine		
mg.	mg.		
0.0 —	100.0 —	—	190.5
10.0 (1.2)	90.0 (10.8)	91.0	184.8
25.0 (2.5)	75.0 (7.5)	90.0	173.0
40.0 (5.0)	60.0 (7.5)	90.0	161.0
53.6 (7.5)	46.4 (6.5)	89.5	148.0
70.0 (10.5)	30.0 (4.5)	90.0	127.0
75.0 (7.5)	25.0 (2.5)	90.0	118.0
82.0 (12.3)	18.0 (2.7)	90.0	107.0
90.0 (13.5)	10.0 (1.5)	89.7	92.2
94.1 (9.5)	5.9 (0.6)	90.0	94.0
100.0 —	0.0 —	—	96.5



Point eutéctique :
90.0°C., 88% de flavone.

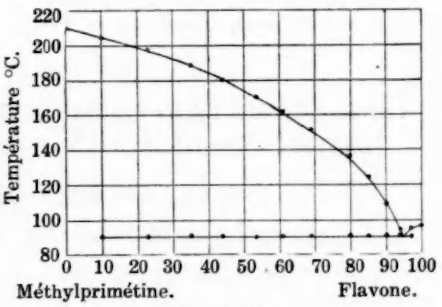
Fig. 3.

(2) W. Nagai et S. Hattori, *Acta Phytochimica*, **5** (1930-1931), 1.

IV. Etude du système: Méthylprimétine (5-oxy-6-méthoxyflavone)[3] et flavone.

Table 4. (Voyez la Fig. 4.)

Pourcentages		Points de dégel °C.	Points de congel °C.
de flavone	de méthyl-primétine		
mg.	mg.		
0.0 —	100.0 —	—	210.5
10.0 (1.0)	90.0 (9.0)	90.5	205.0
22.8 (2.3)	77.2 (7.8)	90.0	198.0
35.0 (3.5)	65.0 (6.5)	91.0	188.5
44.0 (4.4)	56.0 (5.6)	90.5	180.0
53.5 (5.4)	46.5 (4.7)	89.5	170.5
60.8 (6.2)	39.2 (4.0)	90.5	161.5
69.0 (7.8)	31.0 (3.5)	90.6	151.2
80.0 (8.0)	20.0 (2.0)	90.5	136.2
85.0 (10.2)	15.0 (1.8)	90.5	122.5
90.0 (9.0)	10.0 (1.0)	90.5	109.5
94.0 (9.4)	6.0 (0.6)	91.0	94.0
97.0 (9.7)	3.0 (0.3)	90.5	95.0
100.0 —	0.0 —	—	96.5



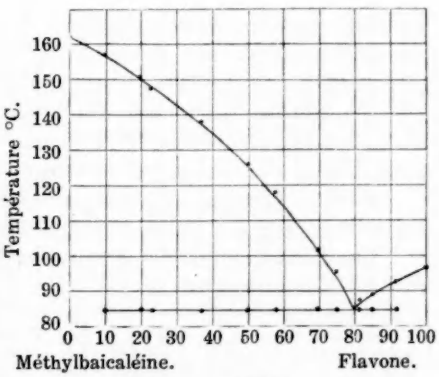
Point eutéctique:
90.5°C., 94.5% de flavone

Fig. 4.

V. Etude du système: Méthylbaicaléine (5,6,7,-triméthoxyflavone)[4] et flavone.

Table 5. (Voyez la Fig. 5.)

Pourcentages		Points de dégel °C.	Points de congel °C.
de flavone	de méthyl-baicaléine		
mg.	mg.		
0.0 —	100.0 —	—	162.0
10.0 (1.1)	90.0 (9.9)	85.0	157.0
19.7 (2.5)	80.3 (10.2)	84.5	150.5
22.9 (2.7)	77.1 (9.1)	84.5	147.5
37.1 (4.3)	62.9 (7.3)	84.5	138.0
50.0 (6.0)	50.0 (6.0)	84.5	125.8
57.7 (6.7)	42.3 (4.9)	84.5	118.0
69.6 (8.0)	30.4 (3.5)	84.5	101.5
75.0 (8.7)	25.0 (2.9)	84.6	95.8
81.3 (10.0)	18.7 (2.3)	84.5	87.5
85.0 (8.5)	15.0 (1.5)	84.5	89.0
91.7 (10.0)	8.3 (0.9)	84.5	92.5
100.0 —	0.0 —	—	96.5



Point eutéctique:
84.6 °C., 79.5% de flavone.

Fig. 5.

En terminant, les auteurs ont l'agréable devoir d'exprimer ses vifs remerciements à MM. W. Nagai et S. Hattori qui les ont aidé par l'envoi

(3) W. Nagai et S. Hattori, *loc. cit.*

(4) S. Hattori, *Acta Phytochimica*, **5** (1930-1931), 108.

de quelques échantillons, et aussi à la Fondation Keimeikai qui leur a donné une part du frais d'expérimentation.

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ÜBER DIE KATALYTISCHE HYDRIERUNG VON UNGESÄTTIGTEN ORGANISCHEN VERBINDUNGEN MIT SELEN.

Von Minoru YOKOYAMA und Munio KOTAKE.

Eingegangen am 28. Januar, 1935. Ausgegeben am 28. April, 1935.

Vor kurzer Zeit haben wir die Tatsache[1] gefunden, dass durch Erhitzen mit Selen einige ungesättigte Verbindungen isomerisiert werden können. Ob jedoch ein derartiges Verhalten für organische Verbindungen allgemein ist, schien uns der Nachprüfung wert und so haben wir als erstes Beispiel Oelsäure mit Selen auf 300°C. unter Umrühren 1–1.5 Stunden lang erhitzt. Die experimentellen Resultate waren ganz anders als wir vermutet hatten, indem nämlich Stearinsäure gewonnen wurde. Es ist nicht undenkbar, dass durch Erhitzen mit Selen ungesättigte Verbindungen reduziert werden. Schon Ruzicka[2] hat durch Erhitzen von Oleanolsäure mit Selen unter Abspaltung von CO_2 und H_2O eine gesättigte Substanz Oleanan gewonnen.

Im weitern haben wir die Einwirkung von Selen auf Elaidinsäure, Ricinolsäure, Linolsäure, Erucasäure und Zimtsäure untersucht und von allen diesen Verbindungen hydrierte Substanzen bekommen.

Daraus können wir ableiten, dass man ungesättigte Verbindungen durch Erhitzen mit Selen ziemlich leicht reduzieren kann.

Die Bedingungen der Erhitzung und die Resultate sind in folgender Tabelle zusammengestellt.

Substanzen		Selen	Temp.	Stunden	Resultate	
Oelsäure	50g.	100g.	300°C.	1.5	Stearinsäure	14g.
Elaidinsäure	3	9	300	1.5	Stearinsäure	0.75
Ricinolsäure	35	70	300	1.5	Stearinsäure	6.8
Linolsäure	46	92	300	1.5	Stearinsäure	11
Erucasäure	36	72	300	1	Behensäure	9.4
Zimtsäure	10	20	310	1	Hydrozimtsäure	1.9

(1) Noch nicht veröffentlicht.
(2) *Helvetica Chim. Acta*, **17** (1934), 442.

UNTERSUCHUNGEN ÜBER DIE KATALYTISCHE OXYDATIONSWIRKUNG KOLLOIDALER SUBSTANZEN. III.

Von Yuji SHIBATA und Kazuo YAMASAKI.

Eingegangen am 31. Januar, 1935. Ausgegeben am 28. April, 1935.

Seit dem Jahre 1918 haben Yuji Shibata, Keita Shibata und ihre Mitarbeiter die Untersuchungen über die oxydasenartige Oxydationswirkung gewisser Metallkomplexsalze fortgeführt,[1] indem u.a. eine interessante Tatsache aufgefunden wurde, dass gewisse Metallkomplexe wie Nickelammine Hydroperoxyd katalytisch zersetzen.[2] Diese Zersetzung erwies sich als eine Reaktion erster Ordnung, genau wie diejenige, die durch Platinsol bewirkt wird.

Angesichts dieses Parallelismus zwischen den Wirkungen der Metallkomplexe und der Metallkolloide bei der Hydroperoxydzersetzung kam man auf den Gedanken, dass die kolloidale Substanzen wie Metallkomplexsalze vielleicht auch die oxydasenartige Oxydation auf Polyphenole leisten vermögen. Zwar wurde diese Tatsache von Y. Shibata und H. Kaneko experimentell bestätigt. In ihren früheren Untersuchungen[3] liessen sie die Hydrosole verschiedener Metalle, Metalloxyde und Silikate auf Pyrogallollösung einwirken, wobei der Reaktionsverlauf mittels eines Spektrophotometers gemessen wurde, da sich Pyrogallol bei der Oxydation bekanntlich rasch braun verfärbt.

Nun haben wir diese Frage wieder aufgenommen, um kennen zu lernen, ob die Oxydation von Phenolsubstanzen durch Metallkolloide auch die Sauerstoffabsorption anzeigen würde. Als kolloidale Metalle wurden hierbei Platin, Gold und Silber verwendet, und wie bei der Oxydationsuntersuchung mit Metallkomplexen wurde der Warburgsche Kapillarmanometer als der Messapparat benutzt.

Diese Experimente ergaben jedoch, dass die Gemische von Pyrogallol und Silber- bzw. Goldsol keine messbare Sauerstoffabsorption zeigten, obzwar dabei die Farbenänderungen der Lösungsgemische deutlich bemerkbar waren. Dagegen absorbierte die Pyrogallollösung, die mit

(1) Die vollständige Literaturangabe findet man in "Untersuchungen über die oxydasenartigen Wirkungen gewisser Metallkomplexsalze. X." von Y. Shibata u. K. Yamasaki, dieses Bulletin, **9** (1934), 2.

(2) Y. Shibata u. H. Kaneko, *J. Chem. Soc. Japan*, **44** (1923), 116.

(3) Y. Shibata u. H. Kaneko, *J. Chem. Soc. Japan*, **45** (1924), 155.

Platinsol versetzt wird, eine bedeutende Menge von Sauerstoff. Es ist sehr interessant zu bemerken, dass die absorbierten Sauerstoffmengen je nach der Bereitungsweise von Platinsol stark verschieden sind.

Beschreibung der Versuche.

Die Oxydationsgeschwindigkeit von Pyrogallol wurde bei 25° mittels eines Warburgschen Manometers gemessen. Das Volum des Reaktionsgefässes beträgt 51.2 c.c. und das Versuchsgemisch bestand aus

Pyrogallol	1/500 Mol	2 c.c.	Hauptraum
30% ige Kalilauge (in Einsatz)		1 c.c.	
Sol		2 c.c.	Ansatzbirne.

Ein gleichartiger Manometer, der im Thermostat neben den Manometer eingestellt wurde, diente zur Bestimmung der Luftdruckschwankung, womit man leicht die beobachtete Druckänderung korrigieren konnte. In jedem Versuch entspricht eine Druckänderung von 1 cm. der Brodie-Lösung einem Sauerstoffverbrauch von 0.04 c.c. Das käufliche Pyrogallol wurde durch wiederholte Sublimation in vacuo gereinigt.

(I) Auto-oxydation von Pyrogallol (Kontrollversuch).

Bekanntlich ist Pyrogallol sehr leicht oxydierbar; daher absorbiert seine wässerige Lösung allmählich den Sauerstoff der Luft. Wir haben also die Sauerstoffmengen, die von Pyrogallollösung ohne oder mit Zusätze von Metallkolloiden absorbiert wurden, in Abb. 1, 2, 3, 4 und 5 dargestellt. Die Ordinaten geben die Druckabnahme in cm. von Brodie-Lösung und auf der Abzisse ist die Zeit in Stunden eingetragen.

(II) Oxydation von Pyrogallol in Gegenwart von Kolloiden.

(1) **Silber.** Die Silbersole wurden nach folgenden Methoden hergestellt: (a) **Reduktion mit Tannin.** Zur Silbernitratlösung wurde Ammoniak zugefügt, bis der einmal gebildete Niederschlag wieder aufgelöst wurde. Zu dieser klaren Lösung wurde eine frisch hergestellte, 1 %ige Tanninlösung zugesetzt. Das so gebildete rotbraune Sol wurde durch Dialyse gegen destilliertes Wasser von Elektrolyten befreit. Der Silbergehalt dieses Sols war 0.040 g. Ag/l. (b) **Die Methode von Kohlschütter.**[4] In eine Flüssigkeit, die das Silberoxyd in Suspension

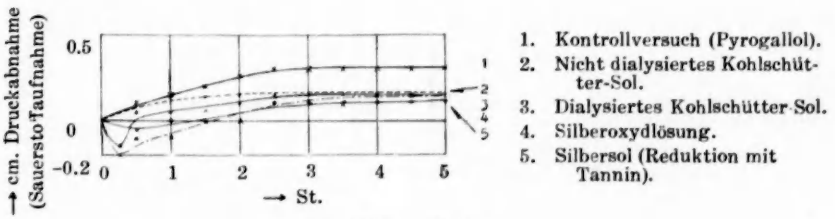
(4) *Z. Elektrochem.*, **14** (1908), 49.

enthält, wurde unter Erwärmung auf 60° ein langsamer Wasserstoffstrom 7 Stunden lang durchgeleitet. Das in Durchsicht gelbbraun und an auffallendem Licht graublau erscheinende Sol, dessen Konzentration 0.071 g. Ag/l. beträgt, wird gegen destilliertes Wasser dialysiert. Die Farbe des Sols veränderte sich dabei zum Rotbraun und der Silbergehalt verminderte sich auf 0.015 g./l. Dieser Verlust an Silbermenge entspricht wahrscheinlich der Menge des Silberoxyds, das durch Dialyse der Lösung entzogen wurde.

Beim Zufügen von nicht dialysiertem Kohlschüttersol zur Pyrogallollösung tritt ein sofortiger Farbenumschlag ins Braun ein und nach einigen Stunden wird eine schwarze Fällung gebildet, dagegen entsteht bei der Verwendung von dialysiertem Sol (sowohl Kohlschüttersol als auch Tanninsol) nur eine schwachgelbe Färbung des Lösungsgemisches, wobei nachher keine Fällung stattfindet. Bei diesen Versuchen erreichte der Sauerstoffverbrauch kaum den Wert des Kontrollversuchs.

Die Niederschläge, die beider Verwendung von nicht dialysiertem Sol gebildet wurden, bestehen aus dem Silbermetall, das wahrscheinlich durch Reduktionswirkung von Pyrogallol auf Silberoxyd gebildet wird. Zum Vergleichszweck wurde die gesättigte Silberoxydlösung zu Pyrogallollösung zugefügt, wobei ein Farbenumschlag ins Dunkelbraun eintrat, ohne dabei keine Vermehrung des Sauerstoffverbrauch aufzuzeigen.

Wie man in Abb. sieht, wurde eine anfängliche Druckzunahme in einigen Fällen beobachtet, was sehr wahrscheinlich durch die lebhafte Entwicklung der Kohlensäure bei der Oxydation von Pyrogallol verursacht wurde.



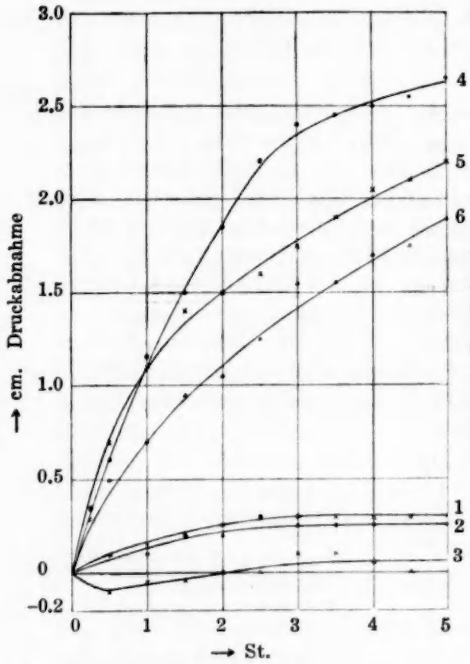
1. Kontrollversuch (Pyrogallol).
2. Nicht dialysiertes Kohlschütter-Sol.
3. Dialysiertes Kohlschütter-Sol.
4. Silberoxydlösung.
5. Silbersol (Reduktion mit Tannin).

Abb. 1. Silber.

(2) **Platin.** Die Platinsole wurden auf folgenden Weisen hergestellt: (a) **Die Bredigsche Methode.** Platin wurde unter reinem Wasser mit Gleichstrom von 100 Volt und 5 Amp. elektrisch zerstäubt. Das so erhaltene schwarzbraune Sol enthielt 0.03 g. Pt/l. (b) **Reduktion mit Formaldehyd.**[5] Eine H_2PtCl_6-Lösung mittels des Gemisches von NaOH

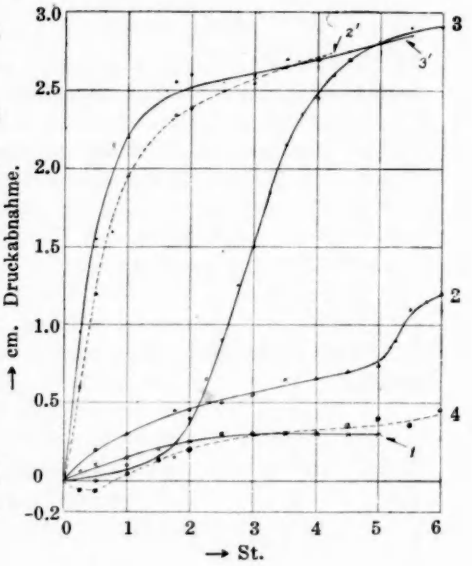
(5) K. Shigena, *Reports Osaka Imp. Ind. Research Lab.*, **8** (1927), 1.

und Formaldehyd in Anwesenheit von Natriumzitrat reduciert und durch Dialyse gereinigt. Die Konzentration war 0.008 g. Pt/l. (c) **Reduktion mit Leuchtgas.**[6] Die Oxydationsflamme des Bunsenbrenners wurde schräg über die Oberfläche der Platinlösung, die sich in einer Porzellanschale befand, gehalten. Nach 10–15 Minuten entstand ein schwarzbraunes Sol, dessen Konzentration 0.037 g. Pt/l. betrug. (d) **Reduktion mit CO.** Ganz neulich haben Sameshima und Sano eine neue Bereitungsmethode von Platinsol veröffentlicht.[7] Leitet man nämlich den Kohlenoxydstrom in eine H_2PtCl_6-Lösung hindurch, so erhält man eine schön



1. Kontrollversuch (Pyrogallol).
2. K_2PtCl_6-Lösung (1.36 g. Pt/l.).
3. H_2PtCl_6-Lösung (0.33 g. Pt/l.).
4. Platinsol (Reduktion mit Formaldehyd).
5. Bredig-Sol.
6. Plationsol (Reduktion mit Verbrennungsgasen)

Abb. 2. Platin.



1. Kontrollversuch.
2, 3, u. 4. Rote Platinsolen (Reduktion mit CO).
2′, 3′. Schwarze gewöhnliche Platinsolen, die beim Stehen von Solen 2 u. 3 im Luft entstanden sind.

Abb. 3. Platin.

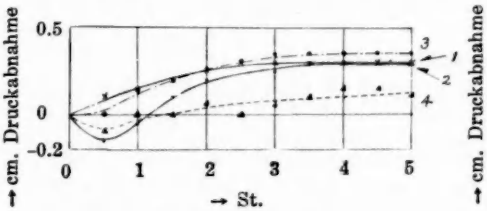
(6) J. Sameshima, *J. Chem. Soc. Japan*, **54** (1933), 695.
(7) Dieses Bulletin, **9** (1934), 320.

tiefrot gefärbte Flüssigkeit. Beim Stehen an der Luft verwandelt sich diese rote Flüssigkeit allmählich ins gewöhnliche schwarze Platinsol (0.03g. Pt/l.). Die zunächst gebildete rote Lösung zeigt manche kolloidale Verhalten, aber ihre Eigenschaften sind noch nicht im näheren bekannt.

Wie man aus der Kurve von Abb. 3 ersieht, gibt die Reaktion dieses roten Sols gegen Pyrogallol sehr unregelmässige und nicht übereinstimmende Resultate, während sich das daraus entstehende schwarze Sol ganz gleich wie andere Pt-Sol verhält. Zum Vergleich wurden H_2PtCl_6– und K_2PtCl_6-Lösung zu Pyrogallollösung zugesetzt, aber man konnte dabei weder Farbenänderung noch Sauerstoffabsorption beobachten.

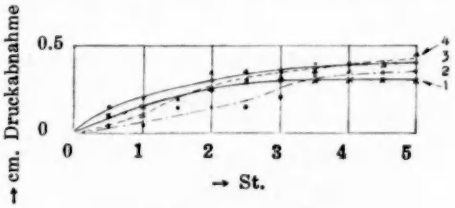
Beim Zusatz von Platinsolen zu Pyrogallol steigt im allgemeinen der Sauerstoffverbrauch und wird gleichzeitig die schwarze Färbung der Lösung hervorgerufen.

(3) **Gold.** Goldsole wurden auch nach verschiedenen Methoden hergestellt: (a) **Reduktion mit Tannin.** Zu 200 c.c. von 0.04%iger Goldchloridlösung wurde 5 c.c. von frisch hergestellter 1%iger Tanninlösung zugefügt. Durch Erwärmung dieses Lösungsgemisches erhielt man ein rot gefärbtes Sol, dessen Konzentration 0.02 g. Au/l. betrug. (b) **Reduktion mit CO.** Das Kohlenoxydgas wurde in Goldchloridlösung eingeleitet. Nach einigen Minuten trat eine Rotfärbung ein. Ihre Konzentration betrug 0.02 g. Au/l. (c) **Reduktion mit Leuchtgas.**[8] Das Goldsol wurde genau in gleicher Weise wie beim Falle von Platinsol hergestellt. Die Konzentration von so erhaltenem Sol war 0.022 g. Au/l. (d) **Die Bredigsche Methode.** Die elektrische Zerstäubung unter reinem Wasser und in KCl-Lösung ($2 \cdot 10^{-4}$ Mol) mit einer Stromstärke von 4–5 Amp. und einer Spannung von 100 Volt (g. S.) ausgeführt. In reinem



1. Kontrollversuch.
2. $HAuCl_4$-Lösung.
3. Goldsol (Reduktion mit Verbrennungsgasen).
4. Goldsol (Reduktion mit Tannin).

Abb. 4. Gold.



1. Kontrollversuch.
2. Bredig-Sol (KCl-Lösung).
3. Goldsol (Reduktion mit CO).
4. Bredig-Sol (reines Wasser).

Abb. 5. Gold.

(8) J. Sameshima, *loc. cit.*

Wasser erhält man nur eine grobdisperse Suspension, die sich nach etwa 30 Minuten am Boden des Gefässes absetzt. Die schwachviolett gefärbte Mutterlauge, deren Goldgehalt 0.01 g. Au/l. war, wurde zum Versuch verwendet. Das in KCl-Lösung dispergierte, tief rot gefärbte Goldsol ist dagegen sehr beständig und die Konzentration betrug 0.014 g. Au/l.

Die Pyrogallollösung, die mit Goldsole versetzt wurde, zeigte keine messbare Sauerstoffabsorption und auch nach langem Stehen keine auffallende Farbenänderung. Schliesslich wurde die Lösung von $HAuCl_4$ (1 g. Au/l.) zur Pyrogallollösung zugefügt, wobei Aurichlorsäure reduciert wurde und sich das Goldmetall in kolloidaler Form in Flüssigkeit dispergierte. Auch dieses blaue Sol zeigte keine Sauerstoffabsorption in Pyrogallollösung.

Zusammenfassung.

Das Oxydationsvermögen von kolloidalem Platin, Silber und Gold auf Pyrogallollösung wurde manometrisch untersucht. Die Platinsole beschleunigten diese Oxydation immer bedeutend, aber Silber und Gold zeigten keine messbaren katalytischen Oxydationswirkungen.

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ON BASKING SHARK LIVER OIL.

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Basking shark (Japanese: "Ubazamé" or "Bakazamé"), *Cetorhinus maximus* (Gunner), reaches to a length of 36 feet and is the largest of all the living fish. The chemical examination of basking shark liver oil was first made by the author[1] in 1917; three commercial specimens, which were apparently prepared from adult fish, contained squalene, and in one of them the author discovered a peculiar iso-octadecane (pristane),

(1) *J. Soc. Chem. Ind. Japan*, **20** (1917), 953, 1099; *J. Ind. Eng. Chem.*, **9** (1917), 1098; **12** (1920), 65.

$C_{18}H_{38}$. Then the author[2] and also Y. Toyama[3] examined the liver oils from young basking sharks (length ca. 2.4–2.7 m.); the former found about 8% of cholesterol in the oil. In France, E. André and H. Canal[4] investigated the oils from two adult and a young basking sharks, and observed a reciprocal relation between the contents of cholesterol and squalene.

Basking shark liver oil is sometimes of peculiar properties, for example, a notable amount of pristane being present in it, so it is one of the most interesting liver oils.

For a long time it had been the author's earnest desire to obtain the liver of the adult fish and to prepare the oil in the laboratory. This was recently fulfilled by procuring the following two specimens.

(1) **Basking Shark Liver Oil No. 1.** The fish which gave this oil was a large female basking shark caught in Toyama Bay[5] on December 14, 1933. It was not dissected at the fishing district, but was sent to Kyoto, where it was exhibited as a show under a signboard of a "large monster sea dragon". As it had been known that the fish would be dissected in the city, several negotiations were made with its owner, and a part of the liver was eventually procured to the laboratory on January 12, 1934, after the lapse of nearly one month.

The fish mentioned above had a length of 775 cm.[6] and a weight of about 2000 kg. The liver had a greyish-white colour mingled with blood-red parts, and was of a very oily consistency; in spite of long keeping in the fish body, it showed a comparatively little putrefaction. A batch of 1000 g. of the liver gave, on complete exhaustion, 854 g. i.e., 85.4% of the oil. From 57 kg. of the liver, 45 kg. (ca. 79%) of the oil was obtained by careful heating.

The oil was a pale orange-yellow liquid with a not unpleasant odour; it deposited a little solid substance at room temperature of 6–14° C. With sulphuric acid it gave a brown colour with a slight violet-red tinge; nearly no blue colouration was observed by the $SbCl_3$ test.

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(2) *Repts. Tokyo Imp. Ind. Research Lab.*, **15** (1920), No. 2, 1, and No. 10, 85.

(3) *J. Soc. Chem. Ind. Japan*, **27** (1924), 601.

(4) *Ann. chim.*, (X), **7** (1927), 69; *Bull. soc. chim.*, (IV), **45** (1929), 598. The lengths of the sharks were 6m., 4.7m., and 3.4m. respectively.

(5) Toyama Bay is an inlet of the Japan Sea and lies to the north of Central Japan, being bounded by Etchu Province (Toyama Prefecture) on the east and south and by Noto Province (Ishikawa Prefecture) on the west.

(6) This figure is due to Mr. Kan-emon Kikuchi of the Toyama High School, who actually measured the fish and to whom the author wishes to express his thanks.

(2) **Basking Shark Liver Oil No. 2.** On January 25, 1934, a telegram from Higashi-Iwase Town Office, Toyama Prefecture, was received by the author, which informed that a large shark was caught again in Toyama Bay. Contrary to the case of the former shark, by easy negotiations and chiefly through the kindness of the above-mentioned office, a part of the liver was procured on January 31. According to a communication of Mr. Awata, a fish-dealer, who treated the shark, it was male in sex, had a length of 24 "shaku" (727 cm.) and a weight of 580 "kwan" (ca. 2170 kg.); the liver weighed 90 "kwan" (337.5 kg.).

The liver was mostly of a dirty, yellowish-grey colour. One kilogram of it contained 838 g., i.e., 83.8% of the oil. From 29 kg. of the liver, about 23 kg. (ca. 79%) of the oil were obtained.

The oil had a pale, orange-yellow colour and did not deposit solids even in winter. Sulphuric acid gave a yellow-brown colour; the $SbCl_3$ test nearly no colouration.

The characteristics, etc., of these oils were found as shown in Table 1.

Table 1.

	d_4^{15}	n_D^{20}	Acid value	Saponif. value	Iodine value (Wijs)	Unsaponif. matter (%)
Oil No. 1 (Female)	0.8973	1.4794	0.16	126.3	185.6	30.35
Oil No. 2 (Male)	0.8808	1.4785	0.21	94.8	191.5	45.13

The oil No. 2 had lower specific gravity and saponification value and higher iodine value. These were chiefly due to the higher proportion of squalene in the oil. The observation that the liver oil of male shark contains more squalene, has already been made in the case of "kurokozamé" (*Centroscyllium*).[7]

(3) **Fatty Acids.** After removing the unsaponifiable matter, the soap solution was decomposed with hydrochloric acid. The fatty acids thus liberated had the properties shown in Table 2.

The fatty acids from the oil No. 2, which contained more squalene, showed a far less unsaturation.

(7) Tsujimoto, *Repts. Tokyo Imp. Ind. Research Lab.*, **27** (1932), No. 15, 20.

Table 2.

Fatty acids from	Appearance	Melt. pt.	Neutr. value	Iodine value	n_D^{25}	Ether-insol. bromide (%)	Br content of the bromide (%)
Oil No. 1	Nearly white crystalline mass	Chiefly melted at 24–25°C., became clear at 27°C.	186.4	130.0	—	27.0	70.23
Oil No. 2	Mixture of white solids and a pale yellow liquid	Became clear at 20–21°C.	179.3	88.2	1.4605	9.3	69.63

(4) Unsaponifiable Matter. Some of the properties are given in Table 3. (Cholesterol was determined by the digitonine method.)

Table 3.

Unsaponif. matter from	Appearance	n_D^{20}	Iodine value	Cholesterol (%)
Oil No. 1	Pale yellow liquid; deposited a little solid substance in winter	1.4900	338.9	1.83
Oil No. 2	Pale yellow liquid	1.4863	302.4	0.94

The lower refractive index and iodine value of the unsaponifiable matter from the oil No. 2 were due to the notable proportion of pristane.

(5) Determination of Hydrocarbons. These were determined by distillation under diminished pressure.[8]

Oil No. 1 (a). The oil (50.3 g.) was distilled under 5 mm. pressure. Above the bath temperature 255°C the distillation began, the thermometer of the flask soon rising to 180°C. At the maximum temperature 247°C. (bath temp. 313°C.) the distillation ended. The distillate was a pale yellow liquid; yield 13.1 g., acid value 2.21. Subtracting the amount of free acids, the yield of hydrocarbons was 25.8%. The refractive index of the distillate, after washing off the acids, was n_D^{20} 1.4897. Its main constituent was squalene. But as an appreciable amount of pristane

(8) Tsujimoto, *J. Ind. Eng. Chem.*, **12** (1920), 71.

appeared also to be present, the lower boiling fraction was determined separately.

Oil No. 1 (b). The oil (50.5 g.) was distilled under the pressure of 5 mm. The distillation began above 250°C. of the bath temperature; the thermometer of the flask soon indicated 144°C. The temperature of the bath was gradually raised to and kept at 270°C., at which nearly no squalene distilled over. The maximum temperature of the distillation was 154°C.; then the temperature sank and the distillation ended. The distillate (colourless liquid) was 1.4 g., and had acid value 1.04. Subtracting free acids, the yield of hydrocarbons (pristane part) was 2.76%. The acid-free substance had n_D^{20} 1.4430 and iodine value 31.8.

Oil No. 2. The oil (50.2 g.) was distilled under 5 mm. pressure. The pristane and squalene parts were determined in one distillation by changing receivers.

Pristane part. Maximum bath temperature 270°C.; maximum distillation temperature 154°C.; distillate (colourless liquid) 3.4 g., acid value 0.202; yield of hydrocarbons 6.76%; the acid-free substance had n_D^{20} 1.4410 and iodine value 18.9.

Squalene part. Maximum bath temperature 320°C.; maximum distillation temperature 246°C.; distillate (nearly colourless liquid) 17.8 g., acid value 0.72; yield of the hydrocarbon 35.34%; the acid-free substance had n_D^{20} 1.4950.

The total yield of the hydrocarbons was 42.1%.

As the above experiments showed, the basking shark liver oils used in the present investigation were notably rich in pristane, especially in the oil No. 2 reaching to about 6%. With such specimens it would not be difficult to prepare pristane in kilogram units, even with ordinary apparatuses of a laboratory. If the total liver of the second shark had been utilized, about 16 kg. (ca. 20 liters) of pristane would have been obtained.

It is also to be noted that the notable occurrence of pristane in basking shark liver oil appears not to be of rare, but of rather frequent instance.

Besides pristane and squalene, there occurred in the oils a new unsaturated hydrocarbon, which is described in the next paper.

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ON A NEW HYDROCARBON IN BASKING SHARK LIVER OIL.

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In the author's first experiments on the isolation of pristane (at that time described by the name of "iso-octadecane"),[1] the crude hydrocarbon even after alkali-washing and redistillation had iodine value 4.4. In Y. Toyama's elaborate investigation on the occurrence of pristane in various squalene-containing shark liver oils, in which the present name has been proposed for the hydrocarbon,[2] the crude substances corresponding to pristane showed always more or less iodine values (2.3–25.6). It should, however, be mentioned that the specimens of shark liver oil used by him were all meagre in the proportions of pristane, the actual yield being 0.5–0.7%, so that in order to separate the hydrocarbon from the oil a strong heating was necessitated. So Toyama judiciously took the unsaturated compounds more likely to be decomposition products rather than normal constituents of the oils. A few years ago the present author[3] got a similar result with "gonshika" liver oil. Thenceforth the author has been inclined to consider the unsaturation or at least a part of it to be due to some naturally occurring substance or substances in the oils. To decide the question it is necessary to procure a shark liver oil that contains pristane in a fairly large proportion. Advantageously the basking shark liver oils reported in the preceding paper are well suited for the purpose.

(1) **Experiment 1.** The basking shark liver oil No. 1 (1500 g.) was distilled under 4.5–5.5 mm. pressure in batches of 300 g. in a Claisen flask, the maximum temperatures of the metal bath and the distillation being 270°C. and 146–152°C. respectively. The yield of the distillate was 31.5 g. (2.1%); it had acid value 1.20. On washing off the free acids with alkali, it formed a nearly colourless liquid of n_D^{20} 1.4400 and iodine value 10.1. It (30 g.) was re-distilled under 14 mm. pressure over metallic sodium in

(1) *J. Soc. Chem. Ind. Japan*, **20** (1917), 1099; *J. Ind. Eng. Chem.*, **9** (1917), 1098.

(2) *J. Soc. Chem. Ind. Japan*, **27** (1924), 333; *Chem. Umschau*, **30** (1923), 181.

(3) *Repts. Tokyo Imp. Ind. Research Lab.*, **26** (1931), No. 10, 33. Gonshika is said to be a very large shark, but its scientific name has not yet been ascertained. The properties of its liver oil closely resemble those of basking shark liver oil.

a small flask; the distillation began at the bath temperature 210°C. Up to the distillation temperature 174°C., 28.6 g. distilled; the distillate had n_D^{20} 1.4395 and iodine value 5.2.

As may be seen from the above-mentioned, the pristane part had, even after purification, an appreciable iodine value. For the separation of unsaturated hydrocarbons from the saturated, a method was tried, which consisted in the application of the greater solubility of the former in alcohol or methanol. This method gave, however, unsatisfactory result, at least with a small quantity of the specimen. As there was no simple method applicable, a final resort was found in the so-called "Bromestermethode",(4) which has been proposed for the separation of saturated and unsaturated fatty acids. Of course, the method has a drawback that it requires energetic chemical reactions, viz., bromination and debromination.

The distillate (25.3 g.) was dissolved in 100 c.c. of ether, and with well cooling in ice, about 0.2 c.c. of bromine was added, thereby no precipitate was formed. On removing the excess of bromine with a solution of sodium thiosulphate and bicarbonate, 26 g. of the bromine addition compound was obtained. It was then distilled under 2.5–3 mm. pressure; the maximum temperature of the bath and the distillation were 188°C. and 142°C. respectively. Contrary to expectation the distillation proceeded continuously without a break, so it was stopped appropriately. The distillation residue was a brown-coloured liquid, which on washing with bicarbonate solution, weighed 1.5 g. It was treated with rasped zinc and alcoholic hydrochloric acid. The reaction went on difficulty. The yield of the debrominated product was 1.1 g., which contained still a little bromine as indicated by the CuO flame reaction. It was an orange-yellow liquid of n_D^{20} 1.4533 and iodine value 64.3. No precipitate was formed on saturating its ethereal solution with hydrogen chloride, so squalene was not present in it.

Although no definite compound was isolated by the above experiment, it has been confirmed that there occur in the pristane part of the basking shark liver oil some natural, unsaturated hydrocarbon or hydrocarbons.

(2) **Experiment 2.** The basking shark liver oil No. 2 was distilled in batches of 300 g. under 3–5 mm. pressure, the maximum temperatures of the bath and the distillation being 270°C. and 139–157°C. respectively. On the whole, 3000 g. of the oil gave 196 g. (6.5%) of the distillate. The

(4) A. Grün, "Analyse der Fette und Wachse", Vol. I, p. 223.

latter was a nearly colourless liquid of acid value 0.3; after alkali washing it had n_D^{20} 1.4400 and iodine value 9.5.

The distillate (195 g.) was redistilled under 9–10 mm. pressure in a flask with a Willstätter bulb. Up to the bath temperature 242°C. and the distillation temperature 175°C., 191 g. of the distillate was obtained. In this distillation the distillate was divided into four fractions to see if some separation of the components be effected. But they had nearly equal refractive indices (n_D^{20} 1.4390–1.4394), so they were mixed together. The distillation residue had n_D^{20} 1.4702 and produced a white precipitate with hydrogen chloride in an ethereal solution; this was probably due to the presence of squalene.

Then the distillate (187 g.) was again distilled under 10.5–11 mm. pressure over metallic sodium; the maximum temperature of the bath was 215°C. and that of the distillation 165°C.; the weight of the distillate 183 g., n_D^{20} 1.4389, iodine value 3.4. The residue also contained a small amount of squalene.(5)

Hereupon the "Bromestermethode" was tried on the refined distillate. It (182 g., 235 c.c.) was dissolved in an equal volume of ether and on cooling 1.3 c.c. of bromine was added. The solution showed a little turbidity and on standing a small amount (ca. 0.1 g.) of a white precipitate was formed, probably due to admixed squalene. The solution was filtered from the precipitate, and washed with a solution of sodium thiosulphate and bicarbonate to remove the excess of bromine. On distilling off the ether, 187 g. of the bromine addition product was obtained (a somewhat larger weight was caused by admixed solvent). It was then distilled under 2.5 mm. pressure; the distillation began at the bath temperature 200°C. Up to the bath temperature 210°C. and the distillation temperature 156°C., 227 c.c. of the distillate was obtained. At this point the distillation was interrupted.(6) The distillation residue formed a dark, brownish-yellow liquid and weighed 7.6 g., which in winter deposited a little solid substance. Debromination was effected with rasped zinc, alcoholic hydrochloric acid and petroleum ether. Difficulty was experienced as in the case of the previous experiment. The debrominated product was a dark, brownish-yellow liquid and amounted to 5.7 g.; by the flame reaction, it was found to contain a little bromine. Finally it was refined

(5) The cause why in these distillations squalene was accompanied in the low boiling fractions was not exactly known.

(6) If we assume the unsaturated hydrocarbon to be $C_{18}H_{30}$, by calculating from the iodine value (3.4), its amount is ca. 6 g. or ca. 8 c.c.; hence the amount of the saturated hydrocarbon corresponds to 235−8=227 c.c.

by distilling under 12 mm. pressure. At 175–185°C., 3.9 g. of a pale yellow liquid distilled over; it had d_4^{20} 0.7948, n_D^{20} 1.4470 and iodine value 66.2. It was free from the halogen, and squalene was not present in it.

(Found: C, 85.46; H, 14.66; Mol. wt. (in benzene), 240. Calc. for $C_{18}H_{36}$: C, 85.62; H, 14.33; Mol. wt., 252.3. Calc. for $C_{18}H_{38}$ (pristane): C, 84.94; H, 15.06; Mol. wt., 254.3.)

The substance was, therefore, recognized to be a mixture of an octadecylene, $C_{18}H_{36}$ (calculated iodine value, 100.6) and pristane, the former predominating.

On the assumption that the substance is a simple mixture of the two hydrocarbons, we get by calculation d_4^{20} 0.8006 and n_D^{20} 1.4510 for the values of the octadecylene (according to Toyama, pristane d_4^{20} 0.7835, n_D^{20} 1.4390). Adopting these values, the molecular refraction of the octadecylene is 84.82, which agrees closely with the calculated value $C_{18}H_{36}$ = 84.86.

The experiment to concentrate the unsaturated hydrocarbon by means of methanol was performed as follows: the mixture (2.105 g.) was treated with 100 c.c. of methanol. The soluble part amounted to 1.331 g. (63.2%) and had n_D^{20} 1.4480 and iodine value 70.3. It (1.209 g.) was again treated with 50 c.c. of methanol. The soluble part was 0.653 g. (54.0%) and had n_D^{20} 1.4500 and iodine value 78.4. The operation was interrupted from the want of the material, but it seemed to be possible to concentrate further the unsaturated hydrocarbon. Of course, the insoluble parts had also fairly high iodine values (1st 43.5, 2nd 51.1).

The concentrated substance (iodine value 78.4) was hydrogenated with platinum black as catalyser. The product was a liquid of n_D^{20} 1.4405 and iodine value 1.9. If hydrogenation be carried out completely, the final product appears to be pristane or a very similar compound.

By the above experiments, the occurrence of an octadecylene in the basking shark liver oil has been confirmed. Its amount was, however, far smaller than anticipated.

The objection that unsaturated hydrocarbons might be formed by the decomposition of the oil by over-heating, may be negated from the following grounds, viz., (1) the temperature of the bath was comparatively low (up to 270°C.), so that no appreciable decomposition would be expected to occur, and (2) decomposition products of the dry distillation of squalene are a mixture of hydrocarbons and not a single compound such as octadecylene. Also according to Toyama's experiments, such products, which correspond to pristane, are highly unsaturated hydrocarbons of very high iodine values.

The octadecylene appears to occur not only in basking shark liver oil, but also in other squalene-containing shark liver oils, probably in far smaller proportions.

Although the author has not yet succeeded in isolating this hydrocarbon in pure state, nevertheless as there is little doubt as to its natural occurrence, he has given the name "Zamene" to it (Japanese: "Samé" or "Zamé" = shark).

Summary.

Although small in proportion, a new octadecylene, $C_{18}H_{36}$, has been found to occur, together with pristane, in basking shark liver oil. In far smaller proportions, it probably occurs in many other, squalene-containing shark liver oils in association with pristane. The author has proposed the name "Zamene" for this new hydrocarbon.

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A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. X. THE VISCOSITY OF AQUEOUS SOLUTIONS OF ELECTROLYTES.

By **Tetsuya ISHIKAWA** and **Toshitomo BABA.**

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Much attention has been paid to the study of the viscosity of strong electrolyte solutions since Jones and Dole[1] proposed in 1929 an empirical equation:

$$\eta^* = 1 + A\sqrt{c} + Bc\,,$$

where η^* is the specific viscosity of a salt solution, c the concentration in mols per litre, and A and B constants. Falkenhagen, Dole, and Vernon[2]

(1) Jones and Dole, *J. Am. Chem. Soc.*, **51** (1929), 2950.
(2) Papers summarized in *Phil. Mag.*, **14** (1932), 537.

made a brilliant success in evaluating the coefficient A from the ion-atmosphere theory in terms of the well-known physical constants, i.e.

$$A = \frac{12.78\times10^{-10}\sqrt{\frac{N}{1000}}\sqrt{\frac{P_1 z_1}{z_1+z_2}}}{\sqrt{4\pi DkT}}\cdot \frac{\varepsilon}{\eta_0}\left\{\frac{z_1^3}{L_1}+\frac{z_2^3}{L_2}-\frac{\frac{4z_1^2z_2^2}{L_1L_2}\left(\frac{L_1}{z_1^2}-\frac{L_2}{z_2^2}\right)^2}{\left[\sqrt{\frac{L_1}{z_1}+\frac{L_2}{z_2}}+\sqrt{(z_1+z_2)\left(\frac{L_1}{z_1^2}+\frac{L_2}{z_2^2}\right)}\right]^2}\right\}$$

where ε is the unit charge of electricity in e.s.u. ($\varepsilon=4.77\times10^{-10}$), N Avogadro's number ($N=6.06\times10^{23}$), P_1 the number of, say, positive ions formed in dissociation, L_1, L_2, and z_1, z_2, the ionic molar conductance and numerical values of the valencies of positive and negative ions respectively, D and η_0 the dielectric constant and the viscosity of the solvent, k Boltzmann's constant ($k=1.37\times10^{-16}$ ergs/degree), and T the absolute temperature.

Wolfenden and his coworkers[3] pointed out that the approximate additivity for individual ions might exist in the coefficient B.

The Falkenhagen-Dole-Vernon theory tells us that the interionic forces acting on the viscosity of electrolyte solutions may become negligibly small as compared with the rapid increase of the viscosity in suitably high concentration, and the Jones-Dole equation which serves at present only for the estimation of the coefficient A in accord with the former theory has no great rôle in an unknown field of more concentrated solutions.

Experimental works on the viscosity of concentrated solutions of various electrolytes have been done in earlier times and have thrown more interesting problems than that of dilute solutions. Hübner[4], Sprung[5], Wagner[6] and others observed the curious phenomenon showing the viscosities less than that of water which they termed "negative viscosity". In fact, some salts of Cs, Rb, K and NH_4 produce negative viscosities. All electrolytes except these show viscosities greater than that of water. The name of "positive viscosity" is often used as an antonym to negative viscosity.

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(3) Cox and Wolfenden, *Proc. Roy. Soc. London*, **145** A (1934), 475; Laurence and Wolfenden, *J. Chem. Soc.*, **1934**, 1144.
(4) Hübner, *Pogg. Ann.*, **157** (1873), 130.
(5) Sprung, *ibid.*, **159** (1876), 1.
(6) Wagner, *Z. physik. Chem.*, **5** (1891), 31.

It is generally observed, however, in the case of the negative viscosity that the viscosity lowers with the increase of concentration more and more in a certain range of concentration, but this tendency suddenly ceases at a suitable concentration, thus showing a minimum value, and at still higher concentration the viscosity increases acceleratedly with the increasing concentration even showing the positive viscosity. The temperature also influences the negative viscosity remarkably in such a manner that it gradually turns out to the positive viscosity as the temperature rises.

In certain cases the inter-ionic forces veil the negative viscosity at extremely low concentration as readily understood from the sign of the sum of the second and third terms in the Jones-Dole equation.

Among many proposed explanations for this anormalous phenomenon of negative viscosity the suggestions made by Jones and Veazay[7] and by Getman[8] are worth mentioning first. These authorities stated that it was due to the cations to lower the viscosity of the solvent while the anions and the undissociated molecules always increased it, and moreover Jones and Veazay pointed out that the salts of K, Rb, and Cs having the highest atomic volumes known showed the marked negative viscosity. Tammann and Rabe[9] who discovered the parallelism between the curve viscosity versus concentration and the curve viscosity versus pressure for aqueous solutions of salts emphasized that the negative viscosity was due to this effect of salts to increase the internal pressure of the solvent. Rabinovich[10] made an extensive study on the cause of the negative viscosity in consideration of many factors acting upon the viscosity of solutions, especially those lowering the internal friction of the solvent, and came to the conclusion that the depolymerization of solvent molecules alone was adequate to explain the negative viscosity and that what was stated by the above-mentioned investigators was self-explaining from this consideration.

Judging from Rabinovich's idea which seems to represent all the explanations hitherto made on this subject, it may be acknowledged that the negative viscosity depends solely on the action of ions—especially of cations, but not on the action of undissociated molecules.

Recently one of the present writers[11] has put forward the assumption that an associated molecule of a liquid is a grouping of single mole-

(7) Jones and Veazay, *Am. Chem. J.*, **37** (1907), 405.
(8) Getman, *J. Am. Chem. Soc.*, **30** (1908), 721.
(9) Tammann and Rabe, *Z. anorg. allgem. Chem.*, **168** (1927), 73.
(10) Rabinovich, *J. Am. Chem. Soc.*, **44** (1922), 954.
(11) Ishikawa, this Bulletin, **4** (1929), 5, 25, 149, 288; **5** (1930), 47, 117; **8** (1933), 280, 293; **9** (1934), 155.

cules which have the self-same dimension with singly existing molecules and the difference between them is no other than the abrupt greatness of the cohesion force of the former in comparison with that of the latter, and has deduced the following viscosity formula for a binary mixture which is fairly calculable from the constants of the constituents provided that no chemical reactions take place on mixing them:

$$\eta = \frac{\eta_1 k_1 a_1 (1-z_m) + \eta_2 k_2 a_2 z_m}{k_1 a_1 (1-z_m) + k_2 a_2 z_m} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

where η, a, k, with suffixes 1 and 2 signify the viscosities, the association degrees and his so called "field constants" of component 1 and 2 respectively; z_m a formal molar fraction of component 2. The above formula indicates that the share of each component viscosity consists of two factors of equal importance, the molecular attraction force presumably proportionate to the association degree and the number of molecules, i.e. it is expressed, in fraction, by $\frac{k_1 a_1 (1-z_m)}{k_1 a_1 (1-z_m) + k_2 a_2 z_m}$ for component 1 or $\frac{k_2 a_2 z_m}{k_1 a_1 (1-z_m) + k_2 a_2 z_m}$ for component 2. The validity of this equation has been already justified with numerous examples of organic non-electrolytes, and has proved to be valid and always superior to other noted empirical equations containing several arbitrary constants. It has also been shown that his equation is fairly applicable to the special case where one of the component is a solid substance such as naphthalene or diphenyl. Ishikawa has made a further success in expressing the viscosity of a binary mixture which forms a molecular compound in solution, i.e.

$$\eta = \frac{\eta_1 k_1 a_1 (1-z_m) + \eta_2 k_2 a_2 z_m}{k_1 a_1 (1-z_m) + k_2 a_2 z_m} + C(1-z_m)^{\nu_1} z_m^{\nu_2} \quad \cdots\cdots\cdots \quad (2)$$

where ν_1 and ν_2 are respectively the molecular numbers of component 1 and 2 in the molecular compound, and C is a constant which varies with the temperature or more closely

$$C = C_0 (\eta_1^{\nu_1} \eta_2^{\nu_2})^{\frac{m}{\nu_1 + \nu_2}}$$

in which C_0 and m are constants independent of the temperature and concentration.

He has also found that m in the above relation takes the value 2 if the molecular compound firmly exists without dissociation, but takes a lower value if the molecular compound suffers ionic or molecular dis-

sociation. Equation (2) has merits that it furnishes us with a reliable means for determining the composition of the molecular compound formed as well as it expresses quantitatively the viscosity of a binary mixture of any kind.

For one more example, the mixture of pyridine (1) and acetic acid (2) will be here adopted from the recent measurements done by Swearingen and Heck[12] over a wide range of temperature. The fusion curve of this mixture studied quite recently by Swearingen and Ross[13] indicated two maxima: one corresponded to a compound $C_5H_5N{\cdot}CH_3COOH$ and the other, a hidden maximum, corresponded probably to $C_5H_5N{\cdot}4CH_3COOH$ or $C_5H_5N{\cdot}5CH_3COOH$ according to their opinion. The curve viscosity versus concentration, however, showed no peculiarity at the former composition, but a marked maximum at the latter.

Now for the estimation of the products ka of the respective liquids we have fortunately the viscosity data at 30°C. of a physical mixture of pyridine and ethyl acetate observed by Puschin and Pinter[14], from which we have evaluated that of pyridine to be 0.76 as referred to that of benzene. Take this value and 0.82 for acetic acid as previously obtained, or put $\frac{k_2a_2}{k_1a_1} = \frac{0.82}{0.76} = 1.08$, which is presumably invariant for the temperature studied, in equation (2). Then the difference between the observed viscosity values (η) and thus calculated (η_0) (η_0^* as appears in other tables means its specific value) can be obtained. Fig. 1 illustrates the values $\eta - \eta_0$ divided by $(1-z_m)z_m$ as ordinate and z_m as abscissa. The horizontal line up to z_m=0.45 indicates the existence of $C_5H_5N{\cdot}CH_3COOH$ which can not be found directly from the curve viscosity versus concentration, and a curve which begins at z_m=0.5 and increases rapidly upwards at higher concentration is the strong indication of $C_5H_5N{\cdot}5CH_3COOH$ as clearly seen from Fig. 2 in which the values $\eta - \eta_0$ divided by $(1-z_m)z_m^5$ is taken as ordinate. The temperature variation of C of these compounds are completely expressed by the following equations respectively:

$$\log C_{1:1} = 1.145 + \frac{1.44}{1+1} \log (\eta_1 \eta_2)$$

and

$$\log C_{1:5} = 3.537 + \frac{2.00}{1+5} \log (\eta_1 \eta_2^5) .$$

(12) Swearingen and Heck, *J. Phys. Chem.*, **38** (1934), 395.
(13) Swearingen and Ross, *J. Phys. Chem.*, **38** (1934), 1085.
(14) Puschin and Pinter, *Z. physik. Chem.*, **151** (1930), 135.

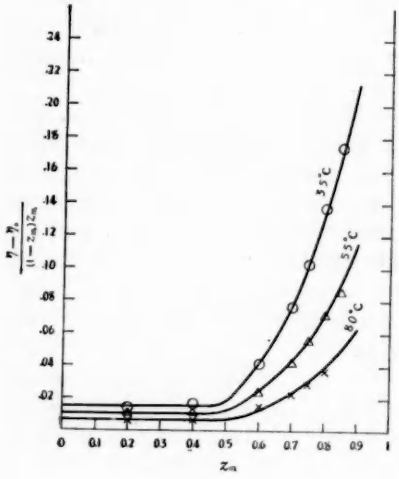

Fig. 1.

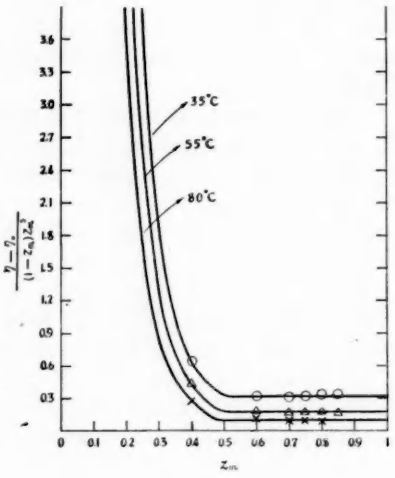

Fig. 2.

The extreme coincidence between the observed and calculated values is shown in Table 1.

Table 1.

t°C.	Molecular compound $C_5H_5N \cdot CH_3COOH$		Molecular compound $C_5H_5N \cdot 5CH_3COOH$	
	$C_{obs.}$ (mean)	$C_{calc.}$	$C_{obs.}$ (mean)	$C_{calc.}$
35	0.0156	0.0155	0.327	0.324
45	0.0129	0.0122	0.235	0.230
55	0.0107	0.0102	0.175	0.177
65	0.0077	0.0087	0.138	0.140
75	0.0074	0.0074	0.108	0.110
80	0.0068	0.0068	0.097	0.096

The present paper is contributed to the study of the viscosity of electrolyte solutions from the same standpoint of view, the Falkenhagen effect being taken into account.

Before entering into further study, the writers have, in this place, to introduce their conception upon the negative viscosity : The chief factor of the negative viscosity depends on no other than the viscosity of the solute or, more correctly to say, the solutional viscosity of the salt, though other investigators considered it to be the depolymerizing action of cations against solvent molecules. As regards the solutional viscosity there have been few descriptions in the literature. Rabinovich supposed it to be of high value enough to compare with the viscosity of

a solid, but Kendall[15] estimated it to be of the same order as that of ordinary organic solvents by using his cube-root formula. Ishikawa also calculated the solutional viscosities of naphthalene and diphenyl to be nearly equivalent as estimated by Kendall, i.e. 0.0265 and 0.0541 at 25°C. respectively. Quite recently Castiglioni[16] observed that camphor and menthol in oleic acid had the solutional viscosities less than the solvent, giving the additional proof for the validity of the Ishikawa formula, although unfortunately we find his mistake in recalculating molar fractions of the solute from its weight percentages: i.e. the solutional viscosity of menthol at 20°C. has the value 0.02596 against the value of the solvent 0.03235 at the same temperature.

It may be probable to consider such a case that the solutional viscosity of a salt differs not so much from the viscosity of water, and if the former is less than the latter, the negative viscosity results according to our theory. The question why the negative viscosity disappears when the concentration sufficiently increases may be easily answered by postulating the solvation or hydration effect as in the pyridine-acetic acid mixture above cited.

In general, the following three cases for the solutional viscosity less than the viscosity of water may be assumed: Firstly, no hydration takes place and negative viscosity is observed throughout the concentration; secondly, a slight hydration takes place so that negative viscosity appears distinctly at low concentration but becomes less distinct or disappears in high concentration; and thirdly, a marked hydration takes place in such a degree that no negative viscosity is perceptible even in low concentration. That when solutional viscosity is greater than the viscosity of water the positive viscosity results is self-evident from the above consideration.

In the following treatment, aqueous solutions of alkali chlorides and nitrates will be taken as adequate examples of the different cases mentioned above.

For simplicity, we rewrite equation (2) in the following form:

$$\eta^{**} = 1 + \frac{(H-1)Kz_m}{1-z_m+Kz_m} + C^*(1-z_m)^{\nu_1} z_m^{\nu_2} \quad \cdots\cdots\cdots \quad (3)$$

where H is the specific solutional viscosity of the solute, the viscosity of water being taken as unity, K a positive characteristic constant of the solute relative to that of water, and C^* a constant independent of the

(15) See Hatschek's "The Viscosity of Liquids", London (1928).

(16) Castiglioni, *Gazz. chim. ital.*, **63** (1933), 395; **64** (1934), 465.

concentration but dependent on the temperature. η^{**} denotes the difference between the observed specific viscosity and the viscosity caused by the inter-ionic forces according to the Falkenhagen-Dole-Vernon theory, though this correction may not be strictly rigorous in high concentration, yet the error thereby may be inappreciable.

Differenciate equation (3) and take the limit when z_m tends to 0, we have

$$\lim_{z_m \to 0}\left(\frac{d\eta^{**}}{dz_m}\right) = (H-1)K + C^{*}\nu_2 \lim_{z_m \to 0} z_m^{\nu_2-1} \quad \cdots\cdots\cdots\cdots \quad (4)$$

As readily seen from equations (3) and (4), since $\lim_{z_m \to 0}\left(\frac{d\eta^{**}}{dz_m}\right)$ is not always negative even when H is smaller than unity unless $C^{*}=0$ or $\nu_2 > 1$, the positive viscosity is not always an indication of H greater than unity, when hydration takes place.

As it has been proved in the previous studies that the value of K is invariant in the small range of temperature, the following two equations at 18° and 25°C. are obtained:

$$\eta_{18}^{**} = 1 + \frac{(H_{18}-1)Kz_m}{1-z_m+Kz_m} + C_{18}^{*}(1-z_m)^{\nu_1} z_m^{\nu_2} \quad \cdots\cdots\cdots\cdots \quad (5)_1$$

$$\eta_{25}^{**} = 1 + \frac{(H_{25}-1)Kz_m}{1-z_m+Kz_m} + C_{25}^{*}(1-z_m)^{\nu_1} z_m^{\nu_2} \quad \cdots\cdots\cdots\cdots \quad (5)_2$$

where suffixes 18 and 25 denote the respective values at 18° and 25°C.

Putting $\frac{H_{25}-1}{H_{18}-1} = q$ and $\frac{\eta_{25}^{*}-1}{\eta_{18}^{**}-1} = r$, we have

$$(\eta_{25}^{**}-1) - q(\eta_{18}^{**}-1) = (C_{25}^{*} - qC_{18}^{*})(1-z_m)^{\nu_1} z_m^{\nu_2}$$

or

$$r = q + (C_{25}^{*} - qC_{18}^{*})\frac{(1-z_m)^{\nu_1} z_m^{\nu_2}}{\eta_{18}^{**}-1} \quad \cdots\cdots\cdots\cdots\cdots \quad (6)$$

In the simplest case where no hydration takes place, equation (6) reduces to

$$r = q = \text{a constant}, \quad \cdots\cdots\cdots\cdots\cdots \quad (7)$$

since C_{18}^{*} and C_{25}^{*} vanish.

Also from equations $(5)_1$ and $(5)_2$ the following equations readily come, if no hydration occurs,

$$\eta_{18}^{**} = 1 + \frac{(H_{18}-1)Kz_m}{1-z_m+Kz_m} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)_1$$

$$\eta_{25}^{**} = 1 + \frac{(H_{25}-1)Kz_m}{1-z_m+Kz_m} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)_2$$

For these special cases, a method of determining the values of H and K has been given in Part V, yet again another will be shown below. Transform, say, equation $(8)_1$, then we obtain

$$\frac{z_m}{\eta_{18}^{**}-1} = \frac{1}{(H_{18}-1)K} + \frac{(K-1)}{(H_{18}-1)K} z_m \quad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

A linear relation exists between $\frac{z_m}{\eta_{18}^{**}-1}$ and z_m, which enables us to find H and K by the use of ordinary graphical method.

Among the salts studied, the three salts CsCl, RbCl, and $CsNO_3$ are found to be good examples of this simple case. They have no hydrates in the studied concentration range and all show the solutional viscosities less than the viscosity of water. The coincidence between the observed and calculated viscosity values are satisfactory as seen from Tables 2, 3, and 4.

Table 2. CsCl.[17]

z_m	18°C.		25°C.		r	
	$\eta_{obs.}^{*}$	η_0^{*}	$\eta_{obs.}^{*}$	η_0^{*}		
0.00448	0.986	0.986	0.992	0.9925	0.64	mean 0.60
0.00893	0.973	0.973	0.985	0.985	0.61	
0.01771	0.952	0.953	0.975	0.974	0.57	
0.03478	0.927	0.927	—	—	—	

$A_{18} = 0.00472$ $H_{18} = 0.8296$ $K = 24.28$
$A_{25} = 0.00489$ $H_{25} = 0.8997$

Table 3. RbCl.[17]

z_m	18°C.		25°C.		r	
	$\eta_{obs.}^{*}$	η_0^{*}	$\eta_{obs.}^{*}$	η_0^{*}		
0.00448	0.990	0.990	0.995	0.995	0.58	mean 0.56
0.00893	0.980	0.980	0.990	0.990	0.56	
0.01771	0.965	0.965	0.983	0.982	0.55	
0.03478	0.943	0.941	—	—	—	

$A_{18} = 0.00472$ $H_{18} = 0.8577$ $K = 21.37$
$A_{25} = 0.00488$ $H_{25} = 0.9194$

Table 4. $CsNO_3$, (Merton).[18]

z_m	18°C.		25°C.		r	
	$\eta_{obs.}^{*}$	η_0^{*}	$\eta_{obs.}^{*}$	η_0^{*}		
0.000419	0.9986	0.9979	0.9988	0.9986	(0.92)	
0.000929	0.9960	0.9949	0.9970	0.9964	(0.81)	
0.001976	0.9899	0.9889	0.9926	0.9918	0.77	mean 0.77
0.002885	0.9844	0.9838	0.9882	0.9881	0,79	
0.004665	0.9752	0.9746	0.9811	0.9811	0.79	
0.006059	0.9681	0.9680	0.9761	0.9761	0.77	
0.008853	0.9561	0.9561	0.9671	0.9671	0.77	
0.01132	0.9470	0.9469	0.9604	0.9601	0.77	
0.01516	0.9347	0.9345	0.9518	0.9508	0.76	

$A_{18} = 0.00486$ $H_{18} = 0.7939$ $K = 33.37$
$A_{25} = 0.00504$ $H_{25} = 0.8415$

(17) Quoted from Internat. Crit. Tab. V.
(18) Merton, *J. Chem. Soc.*, **97** (1910), 2454.

In the cases of $RbNO_3$, KCl, and KI, it is observed generally that r takes a constant value at low concentration, but that it soon rapidly increases or decreases when the concentration reaches a point at which the amount of hydrating molecules begins discontinuously to be appreciable.

Provided that equation (9) is fortunately applicable to these solutions at the concentration range containing no hydrates, it is not difficult to require the composition of hydrates as well as H and K, because the viscosity increase owing to the hydrates can be easily calculated by the use of equation (5), though some ambiguity may exist in the determination of ν_1 unless accurate measurements of viscosities of the wide range of concentration can be had. The calculation thus made are tabulated in Tables from 5 to 7.

Table 5. $RbNO_3$, (Smith, Wolfenden and Hartley).[19]

zm	18°C.					25°C.					r	
	$\eta_{obs.}^*$	η_0^*	$\eta_1^*-\eta_0^*$	$\frac{\eta_1^*-\eta_0^*}{(1-zm)zm^3}$	$\eta_{calc.}^*$	$\eta_{obs.}^*$	η_0^*	$\eta_1^*-\eta_0^*$	$\frac{\eta_1^*-\eta_0^*}{(1-zm)zm^3}$	$\eta_{calc.}^*$		
0.00169	0.9925	0.9920	0.0005	—	—	0.9942	0.9945	-0.0003	—	—	(0.81)	
0.00265	0.9877	0.9873	0.0004	—	—	0.9910	0.9912	-0.0002	—	—	0.75	
0.00342	0.9839	0.9838	0.0001	—	—	0.9885	0.9887	-0.0002	—	—	0.75	
0.00468	0.9785	0.9785	0.0000	—	—	0.9849	0.9849	0.0000	—	—	0.73	
0.00911	0.9628	0.9623	0.0005	—	—	0.9738	0.9733	0.0005	—	—	0.73	mean 0.74
0.00914	0.9623	0.9623	0.0000	—	—	0.9733	0.9733	0.0000	—	—	0.74	
0.01416	0.9483	0.9482	0.0001	—	—	0.9631	0.9631	0.0000	—	—	0.74	
0.01817	0.9410	0.9390	0.0020	(3.4×10^2)	0.9413	0.9588	0.9566	0.0022	(3.7×10^2)	0.9591	0.72	
0.02039	0.9374	0.9347	0.0027	(3.3×10^2)	0.9379	0.9563	0.9534	0.0029	(3.4×10^2)	0.9570	0.72	
0.02737	0.9313	0.9234	0.0079	4.0×10^2	0.9312	0.9542	0.9454	0.0088	4.4×10^2	0.9539	0.69	
0.03495	0.9306	0.9141	0.0165	4.0×10^2	0.9301	0.9572	0.9387	0.0185	4.5×10^2	0.9564	0.65	
0.04187	0.9339	0.9073	0.0266	3.8×10^2	0.9348	0.9639	0.9339	0.0300	4.2×10^2	0.9642	0.59	
				mean 3.9×10^2					mean 4.3×10^2			

$A_{18} = 0.00485$ $H_{18} = 0.8387$ $K = 37.19$

$A_{25} = 0.00498$ $H_{25} = 0.8814$

(19) Smith, Wolfenden and Hartley, *J. Chem. Soc.*, **1931**, 403.

Table 6. KCl.[17]

z_m	18°C.					25°C.					r
	$\eta_{obs.}{}^*$	$\eta_0{}^*$	$\eta_i{}^*-\eta_0{}^*$	$\frac{\eta_i{}^*-\eta_0{}^*}{(1-z_m)z_m{}^3}$	$\eta_{calc.}{}^*$	$\eta_{obs.}{}^*$	$\eta_0{}^*$	$\eta_i{}^*-\eta_0{}^*$	$\frac{\eta_i{}^*-\eta_0{}^*}{(1-z_m)z_m{}^3}$	$\eta_{calc.}{}^*$	
0.00180	0.998	0.998	0.000	—	—	0.999	1.000	-0.001	—	—	(0.79)
0.00448	0.995	0.994	0.001	—	—	0.998	0.999	-0.001	—	—	(0.76)
0.00893	0.990	0.989	0.001	—	—	0.997	0.997	0.000	—	—	0.48
0.01335	0.985	0.986	-0.001	—	—	0.996	0.996	0.000	—	—	0.43
0.01771	0.982	0.983	-0.001	—	—	0.995	0.995	0.000	—	—	0.43
0.02632	0.980	0.978	0.002	(1.0×10^2)	0.981	0.997	0.994	0.003	(1.7×10^2)	0.998	0.35
0.03478	0.982	0.975	0.007	(2.1×10^2)	0.982	1.002	0.993	0.009	2.2×10^2	1.002	0.20
0.04315	0.987	0.973	0.014	1.8×10^2	0.986	1.010	0.992	0.018	2.3×10^2	1.009	-0.12
0.05130	0.994	0.972	0.022	1.7×10^2	0.993	1.021	0.992	0.029	2.3×10^2	1.020	-0.91
0.06725	1.017	0.970	0.047	1.7×10^2	1.018	1.050	0.992	0.058	2.0×10^2	1.054	5.13
				mean 1.7×10^2					mean 2.2×10^2		

mean 0.44

$A_{18} = 0.00484$ $H_{18} = 0.9471$
$A_{25} = 0.00500$ $H_{25} = 0.9765$ $K = 40.39$

Table 7. KI.[17]

z_m	18°C.					25°C.					r
	$\eta_{obs.}{}^*$	$\eta_0{}^*$	$\eta_i{}^*-\eta_0{}^*$	$\frac{\eta_i{}^*-\eta_0{}^*}{(1-z_m)z_m{}^2}$	$\eta_{calc.}{}^*$	$\eta_{obs.}{}^*$	$\eta_0{}^*$	$\eta_i{}^*-\eta_0{}^*$	$\frac{\eta_i{}^*-\eta_0{}^*}{(1-z_m)z_m{}^2}$	$\eta_{calc.}{}^*$	
0.00180	0.9908	0.9907	0.0001	—	—	0.993	0.992	0.001	—	—	(0.79)
0.00448	0.9768	0.9768	0.0000	—	—	0.981	0.981	0.000	—	—	0.84
0.00893	0.9561	0.9561	0.0000	—	—	0.964	0.964	0.000	—	—	0.84
0.01771	0.9228	0.9227	0.0001	—	—	0.936	0.936	0.000	—	—	0.84
0.03478	0.898	0.877	0.021	17.8	0.898	0.915	0.898	0.017	(14.5)	0.919	0.85
0.05130	0.892	0.848	0.044	17.8	0.892	0.916	0.873	0.043	17.1	0.917	0.79
0.08266	0.916	0.802	0.114	18.2	0.912	0.951	0.844	0.107	17.0	0.953	0.63
0.1120	0.978	0.790	0.188	16.8	0.987	1.030	0.826	0.204	18.3	1.021	-0.51
0.1191	1.003	0.787	0.216	17.3	1.007	—	—	—	—	—	—
				mean 17.6					mean 17.5		

mean 0.84

$A_{18} = 0.00481$ $H_{18} = 0.6929$
$A_{25} = 0.00497$ $H_{25} = 0.7420$ $K = 20.20$

It is worth mentioning that there appears to exist in solution as yet unknown hydrates such as $3RbNO_3 \cdot H_2O$, $3KCl \cdot H_2O$, and $2KI \cdot H_2O$, these salts, however, having long been considered to form no hydrates. The reason of the missing of these hydrates depends probably on the neglect because of their small water contents when expressed in weight percentage.

It happens, of course, that in the cases where hydration takes place at zero concentration as are the cases NaCl, LiCl, and $LiNO_3$, no methods of calculating H and K are employable and consequently ν_1 and ν_2 are not determined directly. The determination of ν_1 and ν_2 in such cases, however, may be done by the help of equation (6) as follows.

At first, calculate the values of r i.e. $\dfrac{\eta_{25}^{*}*-1}{\eta_{18}^{*}*-1}$. Remembering that q and $(C_{25}^{*}-qC_{18}^{*})$ are constants, r is linear against the values $\dfrac{(1-z_m)^{\nu_1} z_m^{\nu_2}}{\eta_{18}^{*}*-1}$ provided that the suitable values of ν_1 and ν_2 are taken, and therefore the graphical method is applicable in the determination of the values of ν_1 and ν_2 as well as of q, these values having, of course, to be checked by the relation:

$$\frac{(\eta_{25}^{*}*-1)-q(\eta_{18}^{*}*-1)}{(1-z_m)^{\nu_1}z_m^{\nu_2}} = \text{a constant.}$$

Table 8. NaCl.[17]

z_m	η_{18}^{*}(obs.)	η_{25}^{*}(obs.)	r	$\dfrac{(\eta_{25}^{*}*-1)-q(\eta_{18}^{*}*-1)}{(1-z_m)^{\nu_1}z_m^{\nu_2}}$	η_{25}^{*}(calc.) fr. η_{18}^{*}(obs.)
0.00180	1.0085	1.009	1.059	(0.50)	1.009
0.00448	1.0205	1.022	1.080	(0.58)	1.023
0.00893	1.0405	1.046	1.148	(0.90)	1.045
0.01771	1.0840	1.094	1.127	(0.89)	1.091
0.03478	1.192	1.205	1.071	(0.80)	1.203
0.05130	1.329	1.341	1.038	0.74	1.341
0.06725	1.498	1.509	1.021	0.73	1.509
0.08266	1.700	1.706	1.007	0.75	1.706
				mean 0.74	
				$q = 0.932$	

$A_{18} = 0.00585$ $A_{25} = 0.00601$

Table 9. $LiNO_3$.[17]

z_m	η_{18}^{*}(obs.)	η_{25}^{*}(obs.)	r	$\dfrac{(\eta_{25}^{*}*-1)-q(\eta_{18}^{*}*-1)}{(1-z_m)^{\nu_1}z_m^{\nu_2}}$	η_{25}^{*}(calc.) fr. η_{18}^{*}(obs.)
0.00090	1.0060	1.0060	1.000	—	(1.0064)
0.00180	1.0109	1.0116	1.080	0.44	1.0116
0.00448	1.0259	1.0277	1.075	0.43	1.0277
0.00893	1.0503	1.0534	1.068	0.40	1.0535
0.01771	1.0996	1.1063	1.070	0.42	1.1060
0.03478	1·2110	1.2230	1.058	0.39	1.2226
0.05130	1.341	1.358	1.048	0.41	1.358
0.06725	1.492	1.514	1.046	0.45	1.511
0.08266	1.670	1,694	1.035	0.43	1.692
0.09761	1.874	1.898	1.027	0.41	1.897
				mean 0.42	
				$q = 0.991$	

$A_{18} = 0.00685$ $A_{25} = 0.00696$

The results thus calculated from the viscosity values of the solution of NaCl, and $LiNO_3$ are shown in Tables 8 and 9 with the reference of Fig. 3 for $LiNO_3$. These salts appear to have a hydrate throughout the concentration studied, although the accurate composition of their hydrate may not be hoped for on account of the difficulty of deciding ν_1, yet it may be sure that one and only one molecule of these salts combines with water molecules more than one i.e. hydrates $NaCl \cdot mH_2O$ and $LiNO_3 \cdot nH_2O$, the plausible values of m and n being 2 and 3 respectively. Lowitz[20] obtained $NaCl \cdot 2H_2O$ as a monoclinic crystal, and Mellor[20] mentioned two hydrates $LiNO_3 \cdot 3H_2O$ and $2LiNO_3 \cdot H_2O$, the transition point lying at 29.6°C.

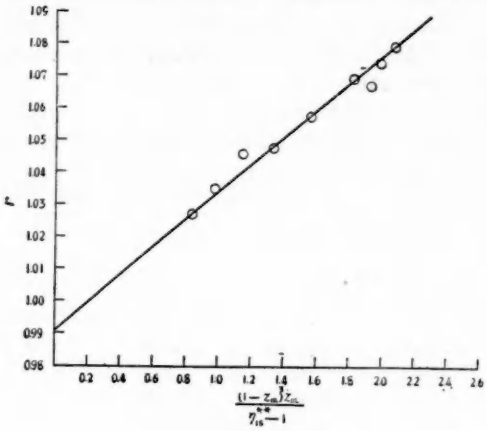

Fig. 3.

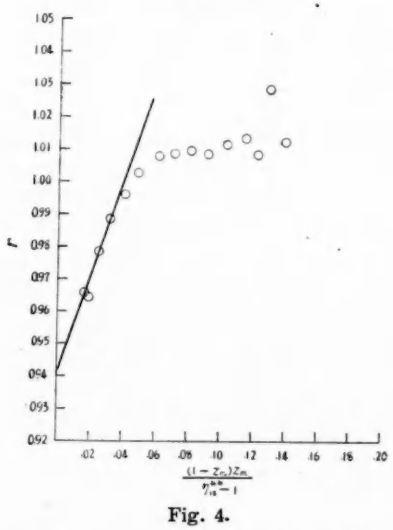

Fig. 4.

With regard to LiCl somewhat different manner is observed as compared with NaCl and $LiNO_3$. The curve r versus $\frac{(1-z_m)z_m}{\eta_{18}^{**}-1}$ in Fig. 4 apparently shows two or more sets of lines, one being distinctly an inclined straight line and others being curved, points, however, lying somewhat complicatedly. The former indicates the existence of a hydrate $LiCl \cdot H_2O$, and the value of q (0.941) obtained from the intersection of this line and the vertical axis may be considered as more reliable than the values obtained from other lines, in which H and K take negative values. Taking this

(20) See Mellor's "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", II, London (1922), 554, 815, 542.

q, we proceed to the further calculation as shown in Table 10. In this case two hydrates more are postulated: $LiCl \cdot 2H_2O$ and $2LiCl \cdot 4H_2O$ besides $LiCl \cdot H_2O$. Bogorodsky[20] obtained three hydrates $LiCl \cdot 3H_2O$, $LiCl \cdot 2H_2O$, and $LiCl \cdot H_2O$, the transition temperature of $LiCl \cdot 3H_2O$ to $LiCl \cdot 2H_2O$ being $-15°C.$, while that of $LiCl \cdot 2H_2O$ to $LiCl \cdot H_2O$ being $12.5°C$. From this reference it may be concluded that in the aqueous solution of LiCl exist two hydrates $LiCl \cdot H_2O$ and $LiCl \cdot 2H_2O$ with this double molecules, but not $LiCl \cdot 3H_2O$ at the temperature range between 18° and 25°C.

Table 10. LiCl, (Green).[21]

z_m	η^*_{18}(obs.)	η^*_{25}(obs.)	Υ	$\frac{(\eta^{**}_{5}-1)-q(\eta^{**}_{18}-1)}{(1-z_m)^{\nu_1} z_m^{\nu_2}}$		η^*_{25}(calc.) fr. η^*_{18}(obs.)
0.0018	1.0136	1.0137	1.009	(0.44)		1.0140
0.0036	1.0271	1.0273	1.008	(0.45)	mean	1.0280
0.0090	1.0692	1.0700	1.013	0.51	**0.63**	1.0711
0.0180	1.144	1.148	1.029	0.69	($\nu_1 = 2$,	1.147
0.0271	1.225	1.227	1.009	0.60	$\nu_2 = 1$)	1.228
0.0362	1.312	1.316	1.014	0.65		1.315
0.0543	1.511	1.517	1.012	0.72		1.513
0.0727	1.747	1.754	1.009	12.8		1.754
0.0912	2.035	2.046	1.010	12.3	mean	2.048
0.1098	2.401	2.413	1.009	12.2	**12.7**	2.417
0.1284	2.878	2.893	1.008	12.9	($\nu_1 = 4$,	2.891
0.1473	3.530	3.539	1.011	13.4	$\nu_2 = 2$)	3.531
0.1663	4.430	4.417	0.9961	13.8		4.403
				(1.33)		(4.431)
0.1854	5.707	5.653	0.9886	1.44	mean	5.652
0.2046	7.550	7.409	0.9786	1.46	**1.43**	7.404
0.2240	10.102	9.777	0.9642	(1.16)	($\nu_1 = 1$,	9.824
0.2289	11.523	11.159	0.9656	1.38	$\nu_2 = 1$)	11.168
					$q = 0.941$	

$A_{18} = 0.00662$ $A_{25} = 0.00665$

As already stated, no method of finding the values of H and K are available in case a solution shows positive viscosity, but even in such a case it is possible only to know whether H is greater than unity or not. Since H is known to become greater as the temperature rises, we may have the following simple relation:

$$\left.\begin{array}{lll} & \text{If } q > 1, & H_{18},\ H_{25} > 1, \\ \text{and} & \text{If } 1 > q > 0, & H_{18},\ H_{25} < 1. \end{array}\right\} \quad \cdots\cdots\cdots \quad (10)$$

(21) Green, *J. Chem. Soc.*, **93** (1908), 2023.

By the use of the criterion it may be obvious that the solutional viscosities of NaCl and LiCl also must be smaller than the viscosity of water. As for $LiNO_3$, q being nearly unity, such decision may not be hoped for, yet H is undoubtedly nearly unity.

From the several examples given above the following conclusion may be reached: The negative viscosity is entirely due to the smaller solutional viscosity of the solute than the viscosity of water, but not to the ionic behaviours suggested by other investigators. The viscosity formula formerly proposed and developed by Ishikawa for a binary mixture of liquids proves to have a general applicability in a new field of aqueous solutions of electrolytes, and at the same time, to play an important rôle in finding their hydrates in solution.

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DIPOLMOMENT DES CHLORWASSERSTOFFES UND LÖSUNGSMITTEL.

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Von zahlreichen Messungen[1] an Dielektrizitätskonstante und Dichte verdünnter Lösungen von HCl, wurde die extrapolierte Molekularpolarisation P bestimmt und daraus das Dipolmoment μ berechnet, wobei die Summe der Elektronen- und Atompolarisation gleich 7.1 angesetzt wurde.

Der Wert des Momentes in Hexanlösung ist, innerhalb des Messfehlers, gleich dem in Gaszustand (1.03×10^{-18}) [2], was wir von der nichtpolaren Natur des Hexanmoleküles von vornherein vermuten können. In Übereinstimmung mit der Beobachtung Fairbrothers[3] haben wir in Benzollösung ein grosses Moment gefunden; Benzol ist makroskopisch sicher nichtpolar, doch mikroskopisch hat es ein starkes Feld, welches ihrgendeine Änderung im HCl-Molekül verursachen kann.[4] In Toluol-

(1) Betr. Messmethode vgl.: Mizushima, Morino und Higasi, *Sci. Pap. Inst. Phys. Chem. Research, Tokyo*, **25** (1934), 159.
(2) Zahn, *Phys. Rev.*, **24** (1924), 400.
(3) Fairbrother, *J. Chem. Soc.*, **1932**, 43; *ibid.*, **1933**, 1541; *Trans. Faraday Soc.*, **30** (1934), 862.
(4) Vgl. auch: Mizushima, Morino u. Higasi, *Physik. Z.*, **35** (1934), 905.

lösung ist das Moment ebenso gross wie das in Benzollösung und der Zunahme des Momentes im Vergleich mit dem in Gaszustand ist in diesem Falle auch dem Benzolkern zuzuschreiben.[4] Obwohl Äthyläther und Chloroform wegen ihrer ähnlichen Werte in Dielektrizitätskostante und in Moment eine analoge Beeinflussung auf den gelösten Stoff erwarten lassen, haben wir dagegen in der Tat einen auffälligen Unterschied zwischen HCl-Momenten in beiden Lösungen gefunden. Während der Wert in Chloroformlösung gleich dem in Gaszustand ist, findet man in Ätherlösung einen beträchtlich grossen Wert, welcher fast gleich der Summe der Momente von Äther und HCl ist. Für das Solvat in der Ätherlösung, wenn es überhaupt ein solches gibt, kann man also ein Gebilde gleichgerichteter Momente vorstellen.

Lösungsmittel	Temp.	P	$\mu\times10^{18}$
Hexan	20	30.0	1.04
Benzol	10	38.7	1.20
„	20	38.5	1.22
„	25	37.8	1.21
Toluol	20	39.5	1.24
Chloroform	30	28.9	1.03
Äthyläther	20	111.3	2.22
Cyclohexan (Fairbrother)[3]			1.32
Benzol (″)			1.26
Tetrachlorkohlenstoff (″)			1.32

Handelt es sich hier um die Änderung der Bindungsart von HCl? Dafür bewährt sich besonders die Berücksichtigung der Placzekschen Auswahlregel[5] in Ramaneffekt. West und Arthur[6] konnten in verdünnter Chloroformlösung die Ramanlinie von HCl beobachten, was mit der bei Dipolmessung beobachteten Tatsache gut übereinstimmt; d.h. die Bindungsart von HCl in der Chloroformlösung ist nichtpolar. Unsere Beobachtung an Ramanspektrum konzentrierter Ätherlösung (Molenbruch von HCl über 40%), die zwar nur vorläufig ausgeführt wurde, zeigt dagegen, dass keine starke Linie von HCl weder einzeln noch mit Ätherlinie überdeckt vorhanden ist. Es ist sehr wahrscheinlich, dass die Bindungsart von HCl in Ätherlösung von derjenigen in Gaszustand verschieden ist. Die Untersuchung an Ramaneffekt wird fortgesetzt und vervollständigt.

Herrn Prof. M. Katayama sowie Herrn Dr. M. Morino danken wir bestens für ihre Ratschläge an dieser Arbeit. Ferner danken wir dem Nippon-Gakujutsushinkôkai, das die zur Durchführung notwendigen Mittel zur Verfügung gestellt hat.

Chemisches Institut der Kaiserlichen Universität zu Tokio.

(5) Placzek, *Z. Physik*, **70** (1931), 84.
(6) West und Arthur, *J. Chem. Physics*, **2** (1934), 215.